AN AUTOMATED VIBRATING-TUBE DENSIMETER FOR MEASUREMENTS OF SMALL DENSITY DIFFERENCES IN DILUTE AQUEOUS SOLUTIONS[1]

L. Hnědkovský[2] and I. Cibulka[2,3]

[1] Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22-27, 2003, Boulder, Colorado, U.S.A.
[2] Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic.
[3] To whom correspondence should be addressed, E-mail: ivan.cibulka@vscht.cz

ABSTRACT

A core of the apparatus is the high-temperature high-pressure densimeter with a metal vibrating tube designed for accurate flow measurements of densities of liquids in the temperature range from 298 to 573 K and at pressures from 0.1 MPa up to 30 MPa constructed in the laboratory. The densimeter is being employed for a study of dilute solutions of aqueous solutions of organic substances where the density difference {solution – water} is a primary experimental quantity. Consequently, partial molar volumes of solutes at infinite dilution in water are evaluated from the measured data. Two sampling sections are connected in series in the filling line of the densimeter. One of them is employed for manual filling of the measured sample into a sampling loop using a syringe. The other section allows fully automated measurement of up to 12 samples in one run. A set of 12 storage bottles is connected to the 1-to-12 switch-over valve. The liquid sample is pumped by a peristaltic pump to the sampling loop through a system of two sampling valves (3x2) that inserts the loop content into the filling line of the densimeter. The pump and valves are controlled by a computer program that also stores the measured data along with necessary information on the measured samples in a data file. The automated measurement of a set of up to 12 sample solutions (each being measured three times) can be completed within about 18 hours. The recorded data are evaluated after the automated run is completed.

KEY WORDS: aqueous solutions; densimeter; density; high temperature; high pressure; partial molar volume.

1. INTRODUCTION

Vibrating-tube densimeters are widely used for measurements of volumetric properties of fluids, particularly liquids. High precision, simple operation, low volume of samples needed, and measurements in a flow regime are main advantages of this method. Besides the commercially available models (A.Paar, Sodev Inc.) there are several densimeters developed and constructed in laboratories over the world and are mostly designed for the use at elevated temperatures and pressures [1-7]. A computer-controlled vibrating tube densimeter was described recently [8]. The well-known principle of the vibrating-tube densimeters is based on mechanical oscillations of a U- or V-shaped glass or metal tube filled with a fluid sample. Oscillations are close to the resonant frequency of the tube and are related to the mass of the tube, i.e. to the density of a fluid filled in. Stationary oscillations of the tube are maintained by the electromagnetic force, generated by means of a drive system, acting on the tube. The input signal for the drive system is obtained from a pick-up system that converts mechanical oscillations of the tube into an electrical signal. The difference between density of a solution, ρ, and that of pure solvent (water), ρ_0, in the vibrating tube is related to the respective periods of mechanical oscillations of the tube, τ, τ_0 , according to the equation, based on a model of the harmonic oscillator,

$$\rho - \rho_0 = K(\tau^2 - \tau_0^2) \qquad (1)$$

where K is the calibration constant dependent on temperature and slightly on pressure. The value of a calibration constant is determined by measurements of the oscillation periods for at least two fluids of known density.

Vibrating-tube densimeters may work in either flow or batch regime. In the flow regime, the standard way of filling the sample into the tube is the use of a sample loop, filled at atmospheric pressure, whose content is, after pressurisation to the experimental pressure, inserted into the filling line using a valve. In a batch mode the densimeter is usually filled with a sample at atmospheric pressure and the sample is then pressurised to experimental pressure. It is, however, advisable to keep the pressure inside the tube constant and thus avoid pressure changes that may cause the drift of the oscillation period.

2. EXPERIMENTAL APPARATUS

2.1. Vibrating-tube densimeter

A vibrating-tube densimeter designed for measurements in the temperature range from 298 to 573 K and at pressures from 0.1 MPa up to 30 MPa is described in detail elsewhere [9]. A metal (Hastelloy C) vibrating tube is fixed to the thermostated block of the cell located inside two thermostated jackets and the entire assembly is placed in a vacuum chamber to minimize heat losses. The lid of one of the jackets serves as a pre-heater to bring the temperature of a flowing sample to the temperature close to that of the block of the measuring cell. The driving system is based on passing the driving electrical signal directly to the electrically insulated vibrating tube whose tip is located in the magnetic field of a strong permanent magnet. The photo-electric pick-up system employs

glass-fiber optics passing through the magnet extenders. Nitrogen and water is used for calibrations at each temperature and pressure. Short-term fluctuations of temperature of the densimeter cell are within 1 mK. The maximum systematic error of the measured density differences {ρ(solution) - ρ(water)} resulting from the densimeter calibration is about 0.15 per cent and the reproducibility of the measurements is $\pm 5 \cdot 10^{-3}$ kg·m^{-3}.

The densimeter is incorporated in the filling line [9, 10] that was several times modified. The present stage of the line is shown schematically in figure 1. Degassed water from a boiler WB is pumped using a high-pressure liquid chromatography pump HPLC through the sampling devices (manual MS and automated AS) into the densimeter and then pushes the compressed nitrogen from the waste container WC into the thermostated back-pressure regulator BPR (a type with the gas dome). Adjustment of the temperature of the regulator within ±0.1 K minimizes pressure fluctuations in the line caused by the changes of laboratory temperature and enables a fine adjustment of pressure in the line. No waste liquid flows through the regulator. Thus it is protected from corrosion and the damping effect of gaseous nitrogen in the container WC

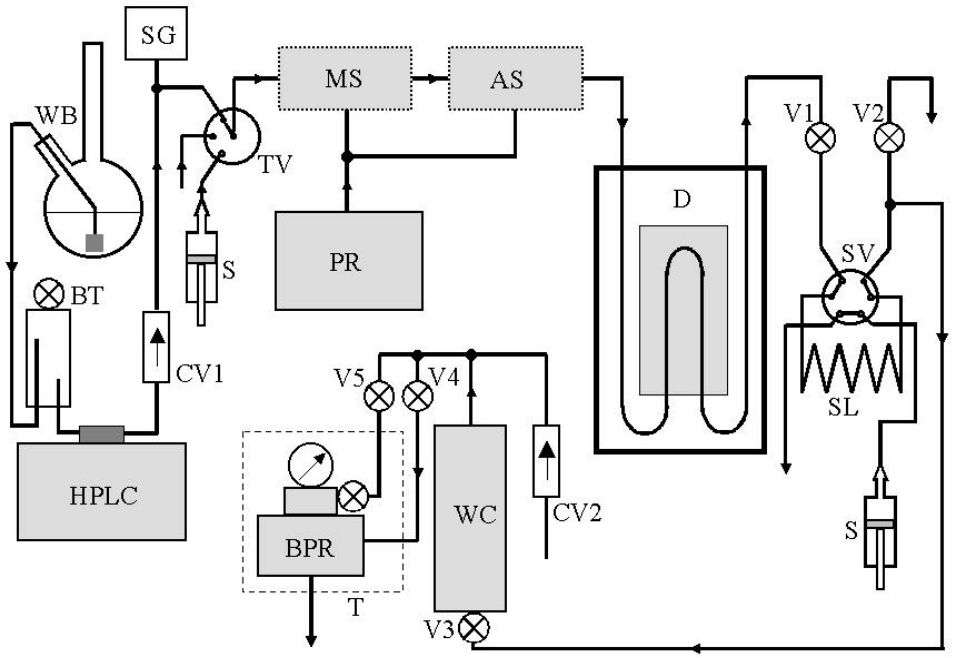

Figure1. Schematic diagram of fluid delivery and pressure system.
WB – boiler with distilled and demineralized water; BT – bubble trap; HPLC – high-pressure liquid chromatography pump; CV1, CV2 – check valves; TV – three-way switching valve; S – syringe; SG – strain pressure gauge; MS – manual sampling block (see Fig.2); AS – automated sampling block (see Fig.3); D – densimeter; SL, SV – sampling loop and a valve; WC – waste liquid container (volume 1 dm^3); BPR – back-pressure regulator; T – thermostat of BPR; V1 to V5 – shut-off valves.

eliminates slight pressure pulses produced by the HPLC pump. Fluctuations of pressure in the line are less than ±0.03 MPa, typically ±0.01 MPa. A sampling loop SL may be used to withdraw the samples of the liquid passed through the densimeter and thus the checks of decomposition of the samples are possible. Auxiliary pump PR serves for pressurization of the sample loops (see below) to the pressure close to that in the line. This avoids any sudden pressure changes in the line after a sample is inserted into the flow of compressed water. Three-way switching valve TV is used for filling either nitrogen (one of the calibrating fluids) or a cleaning liquid into the line.

2.2. Sampling devices

There are two sampling devices connected in the series in the filling line (Fig.1). A manual one (Fig.2) enables to employ one of two sampling loops for inserting the sample into the flow of water. The liquid samples are filled into the loop(s) from syringes and the valves V1 and V2 are operated manually. Two sampling loops can be used simultaneously when a sample non-miscible with water (generally with a carrier fluid delivered to the system from the high-pressure pump) is measured. In this case an intermediate liquid miscible with both water and the sample is filled into the loop SL1 and the sample from the loop SL2 is inserted into the flow of this intermediate liquid.

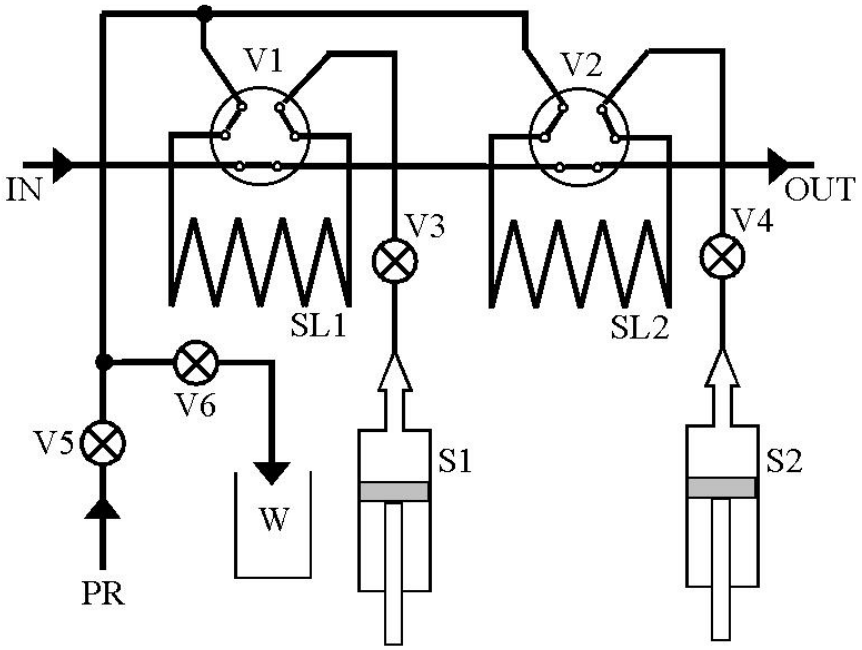

Figure2. Manual sampling block (MS in Fig.1).
SL1, SL2 – sampling loops; S1, S2 – syringes; V1, V2 – sampling valves; W – waste; PR – pressurization of the sample loops; V3 to V6 – shut-off valves.

It is obvious that the experimenter's work is rather time-consuming and routine consisting of filling the sample loops, operating the valves and recording data. Therefore an automated sampling device (Fig.3) was developed recently which minimizes the experimenter's effort. A set of up to twelve storage bottles SB (SB1 to SB12, only two are shown in the figure) containing measured samples is placed on the metal plate CP, which is cooled using two Peltier units to the temperature slightly below the temperature of the laboratory. Cooling of the plate minimizes condensation of vapor on the inner surface of the bottles and reliable corrections of the solution concentration with respect to evaporation can be evaluated. Samples in the bottles are under slight overpressure of argon that enables measurements of samples sensitive to air. The sample from the particular bottle (SB1 in the figure) is pumped into a sampling loop SL via sampling valves V1 and V2 in the LOAD position using a peristaltic pump PP. After the sampling loop is filled with the sample (allowing the previous sample to be washed out) the valve V1 is switched into the INJECT position and the content of the sampling loop is pressurized to the pressure close to experimental pressure using auxiliary high-pressure pump (PR). During the above procedures degassed water from a high-pressure pump flows into the densimeter and the water baseline is recorded. Then the valve V2 is

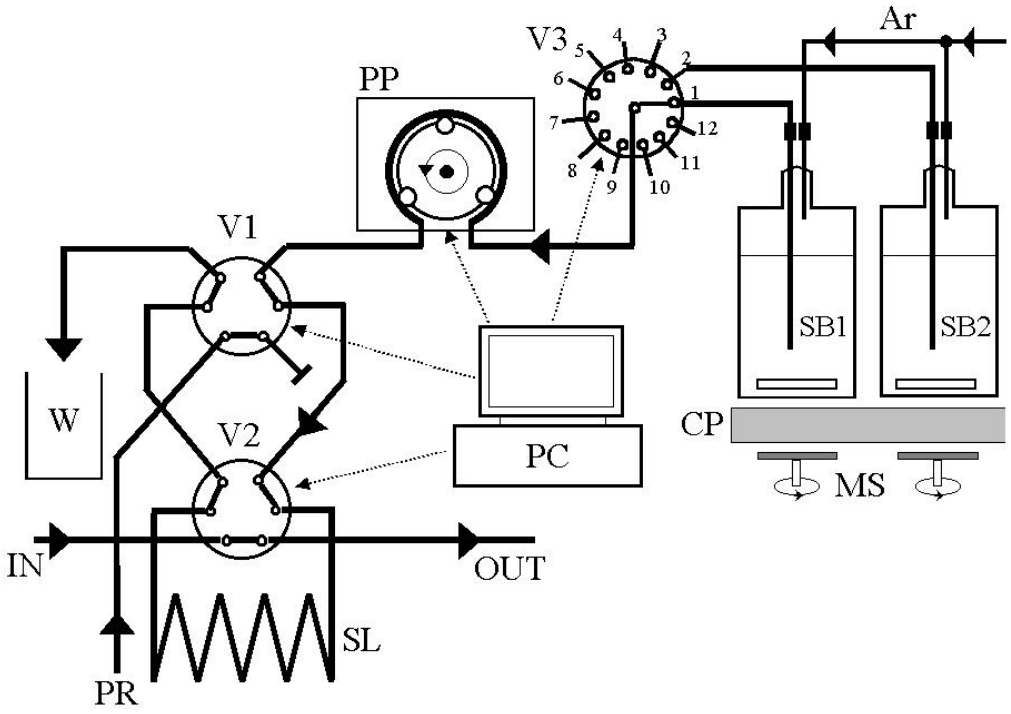

Figure 3. Automated sampling block (AS in Fig.1).
V1, V2 – sampling valves (3x2); V3 – one-to-twelve switch-over valve; SL – sampling loop; PC – personal computer; PR – pressurization of the sample loop; PP – peristaltic pump; W – waste; SB1, SB2, ..., SB12 – storage bottles with samples (only two bottles are shown); CP – cooled plate; MS – magnetic stirrers; Ar – inlet of argon under slight overpressure. The positions of valves shown in the figure (V1 and V2 in LOAD position, V3 switched to SB1) correspond to the stage of filling the sample loop with sample 1.

switched into the INJECT position, the sample from the sampling loop is pushed out from the loop into the densimeter and the sample plateau is recorded. The valve V3 is then switched over to the next position, valves V1 and V2 are switched into the LOAD positions and the procedure is repeated for the next sample. The valves (V1, V2, V3) and the peristaltic pump are controlled by a computer (PC). The automated run with twelve samples, each being measured three times (three consecutive cycles of measurements of all twelve samples), takes about 18 hours. Since the goal experimental quantity is the difference between density of a solution and that of water, a bottle with water is always one of those connected to the automated apparatus and the density difference is evaluated as the difference between density of a solution and density of water, both saturated with argon. The presence of dissolved argon causes a change of density ranging from $+5 \cdot 10^{-3}$ kg·m^{-3} at 298 K to $-2.5 \cdot 10^{-2}$ kg·m^{-3} at 573 K. This effect might be regarded as similar for dilute aqueous solutions and pure water, and therefore the density difference employed for evaluation of partial molar volumes is not affected.
The computer (PC) serves not only to control the automated sampling device but it also records all necessary data from the densimeter (real time, oscillation period of the vibrating-tube, temperature, pressure). The data are written into a file and evaluated after the automated run is completed. A typical record for twelve samples is shown in figure 4. Water and eleven samples of dilute solutions of two organic solutes (ethanol)

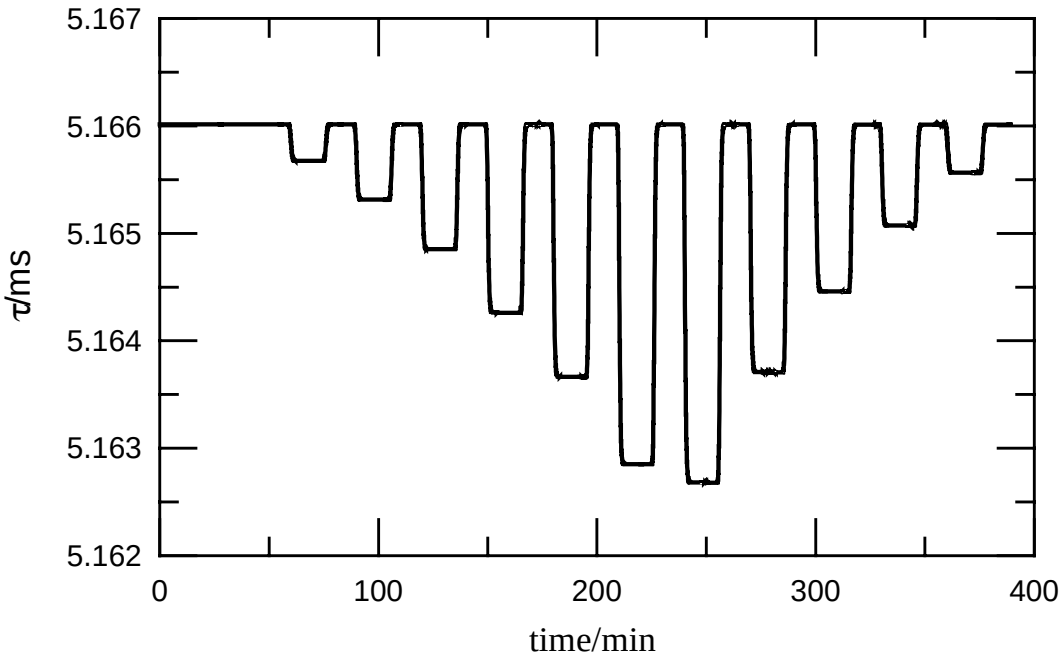

Figure 4. Time record of the period of tube oscillations τ for an automated run with twelve sample bottles (only one round over the bottles is shown).
First sample was water saturated with argon (the change of the period is not visible in the figure due to small density difference), followed by six samples of aqueous ethanol in the order of increasing concentration and five samples of aqueous 1-propanol in the order of decreasing concentration. Flow rate of the liquid in the delivery system was 0.6 cm^3·min^{-1}.

and 1-propanol) in water were installed into the sampling device. The samples were connected to the valve V3 (Fig.3) in the order with minimal differences in concentration between consecutive samples. Usually three rounds are performed within one run, i.e. each sample is measured three times.

3. CONCLUSION

Substantial advantages of the automated sampling apparatus are as follows: i) it operates without any assistance of an experimenter (usually overnight); ii) it enables to have the samples under inert atmosphere which might be important for measurements of solutes sensitive to air; iii) since the storage bottles are never opened (the bottles containing prepared solutions are stored with the lids with both tubes closed), the corrections of concentration related to the evaporation of the samples in the bottles can be evaluated with a high reliability even for volatile solutes. On the other hand, only samples miscible with water can be measured automatically using the present arrangement.

ACKNOWLEDGMENTS

This work was supported by the Czech Ministry of Education, Youth and Sports (fund MSM223400008).

REFERENCES

1. H. J. Albert, R. H. Wood, *Rev. Sci. Instrum.* **55**: 589 (1984).
2. R. H. Wood, C. W. Buzzard, V. Majer, *Rev. Sci. Instrum.* **60**: 493 (1989).
3. J. M. Simonson, C. S. Oakes, R. J. Bodnar, *J. Chem. Thermodynamics* **26**: 345 (1994).
4. J. G. Blencoe, S. E. Drummond, J. C. Seitz, B. E. Nesbitt, *Int. J. Thermophys.* **17**: 179 (1996).
5. R. F. Chang, M. R. Moldover, *Rev. Sci. Instrum.* **67**: 251 (1996).
6. C. Xiao, H. Bianchi, P. R. Tremaine, *J. Chem. Thermodynamics* **29**: 261 (1997).
7. V. Hynek, M. Obšil, V. Majer, J. Quint, J.-P. E. Grolier, *Int. J. Thermophys.* **18**: 719 (1997).
8. E. C. Ihmels, C. Aufderhaar, J. Rarey, J. Gmehling, *Chem. Eng. Technol.* **23**: 409 (2000).
9. V. Hynek, L. Hnědkovský, I. Cibulka, *J. Chem. Thermodynamics* **29**: 1237 (1997).
10. J. Jedelský, L. Hnědkovský, I. Cibulka, *J. Chem. Thermodynamics* **31**: 27 (1999).